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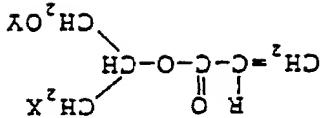
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(57) Polyurethanes and polyurethane/polyureas crosslinked using 2-glyceryl acrylate or 2-glyceryl methacrylate.
 (57) A crosslinkable polyurethane or polyurethane/polyurea comprises the reaction product of a composition comprising a macrodial or macrodiamicine, 2-glyceryl acrylate or 2-glyceryl methacrylate, a diisocyanate, and optionally a small glycol or small diamine as chain extender. The performance properties of the polyurethanes and polyurethane/polyureas can be controlled by adjustment of the crosslink level and/or curing parameters.

wherein R is hydrogen or methyl



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represented by the formula:

The preparation of readily solvolyzable polymers of the classes of monomers disclosed is 45 polyesters is described in U.S. Patent No. 4,578,504. One of the classes of monomers and

Ezrelev and Arbu佐va did not teach or suggest the use of 2-glyceryl methacrylate monomer.

isopropylidene glyceryl methacrylate. The ketonic protection was removed from the monomer units by either acid hydrolysis, or preferentially, by alcoholysis and the resultant polymer was used to prepare hydrogels.

A Russian publication (Chem. Absts. No. CA90(14):104388) Vysokomol. Soedin., Ser. B, 20(10), 77-9 by 40 Ezrelev and Arbu佐va, describes linear polymers of glycerol monomethacrylate(PMG) obtained from (modulus) for use in binder systems for magnetic tape.

U.S. Patent 4,467,078 describes improved electron beam curable polyurethane compounds having a greater range in degree of cure, consequently providing systems with a greater range of hardness 35 prepolymers of hydroxyl terminated polymers with hydroxyl terminated acrylates or alkylacrylates.

(2) acrylate or alkacrylate terminated polyurethanes prepared by reacting isocyanate terminated having terminal hydroxyl and unsaturated groups or terminal hydroxyl and pendant unsaturated groups and

from a mixture of (1) polyurethanes prepared from polymeric polyols, organic diisocyanates and polyethers U.S. Patent 4,446,286 describes improved electron beam curable polyurethane compounds obtained 30 for magnetic tape.

U.S. Patent 4,408,020 describes polyurethanes having terminal hydroxyl and pendant unsaturated groups. These polyurethanes are electron beam cured to form useful binder systems

diisocyanates and polyethers having terminal hydroxyl and unsaturated groups or terminal hydroxyl and 35 pendant unsaturated groups. These polyurethane resins containing ethylenic side groups.

U.S. Patent No. 4,366,301 describes acrylic or methacrylic acid ester of a trihydrolic alcohol, preferably the known compound 2,3-dihydroxypropyl acrylate (also called 1-glyceryl acrylate), as

the unsaturated diol for crosslinking thermoplastic polyurethane resins.

U.S. Patent 4,080,200 describes polyurethanes by crosslinking the polymer either thermally (with or without 40 thermal initiator additives or via ultraviolet light, gamma or accelerated electron radiation).

improved or extended in industrial applications, service temperature limits, and utilities of such materials may often be 45 modulus. In addition, the properties, service temperature limits, and enhanced mechanical properties, such as tensile and separation observed in polymer systems leads to formation of a "soft" and "hard" two-phase microstructure. This phase

incompatibilities between the "hard" and "soft" components, these materials may undergo phase-separa- 50 tion in the solid-state resulting in the formation of a glassy or semicrystalline nature ("hard" segment). Due to

rubber ("soft" segment) while the other is of a glassy or semicrystalline nature ("hard" segment). Due to 55 segments of chemically different units. At service temperatures, one of the segments is generally viscous or

nature of these materials. The polyurethanes and polyurethane/polyureas are composed of blocks or

considered the materials of choice in such applications, often directly related to the block-copolymer 60 materials in a variety of industrial applications; the mechanical and physical properties for which they are

Polyurethanes and polyurethane/polyureas are widely employed as high performance engineering

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Background of the Invention

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polyurethane/polyureas and methods for their preparation and to articles made from the polymers. In another aspect, the invention relates to controlling the performance properties of the polymers by

adjustment of the crosslink level and/or curing parameters.

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Technical Field

POLYURETHANES AND POLYURETHANE/POLYUREAS CROSSLINKED USING 2-GLYCERYL ACRYLATE OR 2-GLYCERYL METHACRYLATE

The novel polyurethanes or polyurethane/polyureas of the invention and the methods for their preparation utilize 2-glyceryl acrylate or 2-glyceryl methacrylate (formula I) as a chain extender to allow selective and controllable crosslinking of the resultant polymer. The polymethylizable compositions also contain macrodiols which may be, for example, polyester or polycaprolactone carbinols or silicocene carbinols or macrodiamines (formula II), which may be, for example, polydimethylsiloxane diamines. In addition, other small glycols or diamines (formula III) can be present, optionally, as additional chain extenders. Finally, organic disocyanates are present in the polymethylizable composition. Upon application of heat the linear polyurethanes and polyurethane/polyureas are provided. Application of additional energy,

Detailed Description of the Invention

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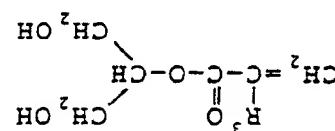
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15 Briefly, the present invention provides a crosslinkable polyurethane or polyisocyanate/polyisocyanate composition comprising
the reaction product of a composition comprising a macrodioil or macrodiisocyanate, 2-*g*-glyceryl acrylate or 2-*g*-glyceryl methacrylate,
glyceryl methacrylate (also called 1,3-dihydroxy-2-propyl (meth)acrylate), a diisocyanate, and, optionally a small glycol or diamine.
In another aspect, a crosslinked polyurethane or polyurethane/polyurea is provided by thermal, radi-
ation, or electron beam cure of the crosslinkable polyurethane/polyureas of the invention generally have number average
molecular weights in the range of 10,000 to 400,000.
20 Crosslinkable polyurethanes or polyurethane/polyureas of the invention generally have number average
molecular weights in the range of 10,000 to 400,000.
The present invention provides the design, synthesis and incorporation of acrylics and methacrylics
into crosslinkable polyurethanes which can be made into articles of manufacture
and which allow optimization of the performance/polyureas such articles via adjustment of the type
or ratios of reactants and adjustment of the level of crosslinking in the type
of polyurethane/polyurea.
25 The present invention provides a controllable method for adjustment of crosslinking of polyurethanes
and polyurethane/polyureas. This is accomplished utilizing 2-glyceryl acrylate or 2-glyceryl methacrylate,
and polyurethane/polyureas. This is a controllable method for adjustment of crosslinking of polyurethanes
and polyurethane/polyureas. This is a controllable method for adjustment of crosslinking of polyurethanes
and polyurethane/polyureas.

Summary of the Invention

$$\text{CH}_3(\text{CF}_2)_n\text{C}=\text{O}^- \quad \text{trialkylsilyl of the formula} \quad [\text{CH}_3(\text{CH}_2)]_3\text{Si}-.$$

wherein X is perfluoralkylsulfuroxy, perhaloacyloxy, benzoyloxy, or trialkyloxyl, or trifluoroacetoxy.

X is tluoro, chlorine, bromo, iodo, hydroxyl, perfluorooxy, perfluoralkyisulfonoxyl or trifluorooxy of one to three carbon atoms or perfluorooxy of one to three carbon atoms, benzoyloxy, and trichlorosacetoxyl; Y is trichloroacetyl, perfluorooacyl or the formula

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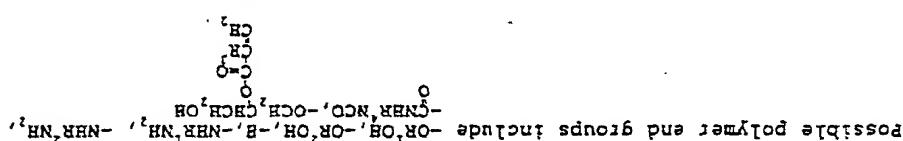
The method of the invention is shown in the flow chart below:

either thermal (with or without a thermal initiator) or ultraviolet light, gamma radiation or electron beam radiation, converts the linear polyurethane or polyurethane/polyurea into a crosslinked network. The crosslinked polyurethane or polyurethane/polyurea polymers of the invention are useful for preparing materials of use in areas including flexible magnetic recording media binders, biomaterials, wound dressing materials, membranes, membrane applications (waterproof fabric treatments), and protective coatings.

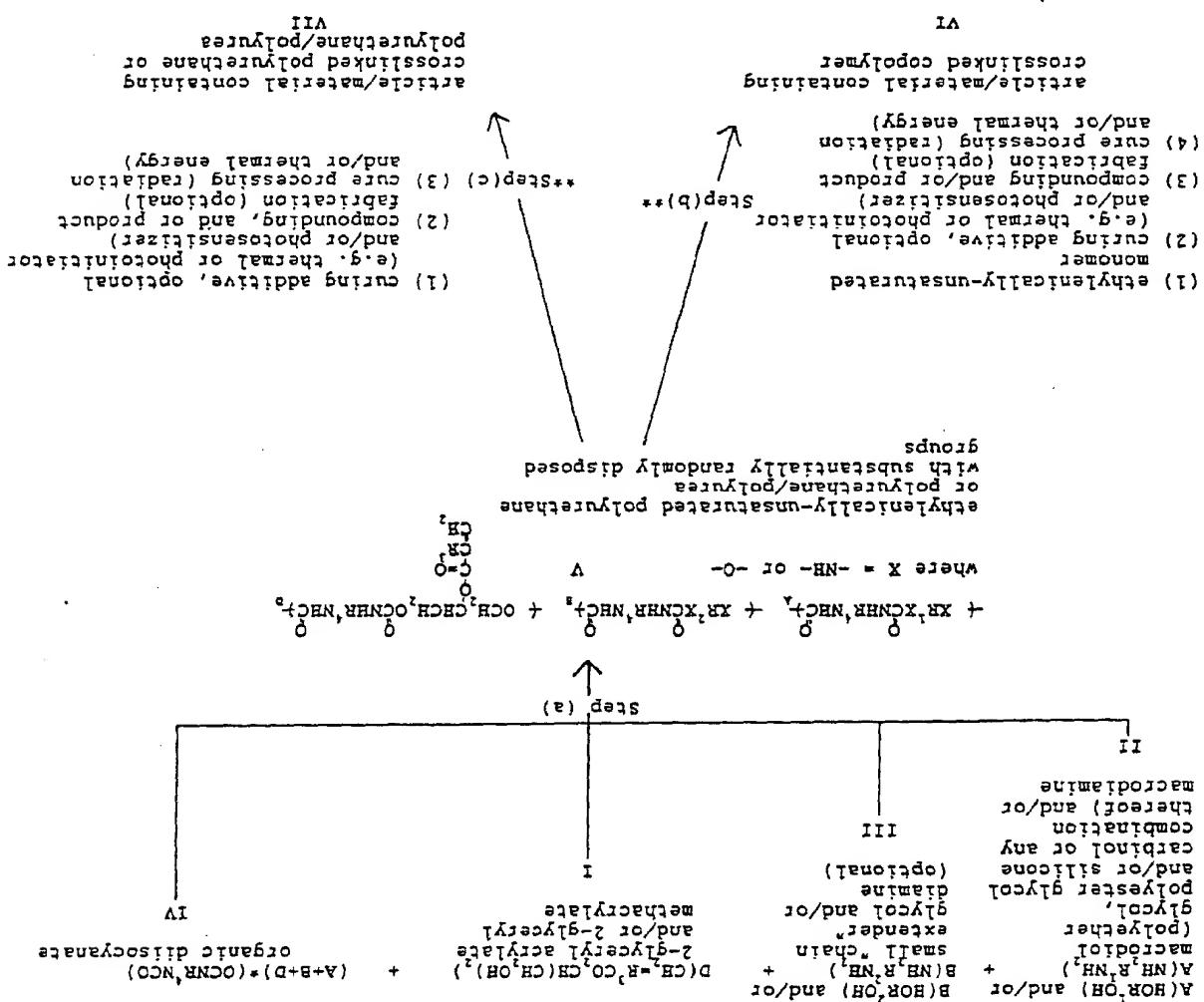
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* * * The order of the sub-steps may be modified.

For 10 mole percent excess NCO equivalents, the total number of OH end-groups above, i.e., these can be up to 10 equivalents per molecule.



R₂'', independent allylene, cycloalkylene, alkylene, substituted-alkylene or any combination thereof, may be hydrogenated-cycloalkylene, substituted-alkylene or any combination thereof, R₂, as a polyester or a polyesters or a polydimethylsiloxane segment having a molecular weight of about 230 to 10,000.



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Example 2

To a cold ($0\text{--}5^\circ\text{C}$) solution of 300g (1.43 mole) of trifluoracrylic anhydride in about 1 liter of dichloromethane was added dropwise 170g (1.2 mole) of glycidyl methacrylate and stirring continued at about $0\text{--}5^\circ\text{C}$ for approximately 1 hour after completion of the addition. The reaction mixture was allowed to stir at ambient temperature for about 20 hours, after which time the dichloromethane was evaporated in vacuo to provide a colorless residue. The product was distilled at $70\text{--}75^\circ\text{C}/0.3\text{ mm}$ of mercury. Structural assignment was confirmed by infrared and nuclear magnetic resonance spectral analysis.

Preparation of bis(trifluoracetoxyethyl)methyl methacrylate

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Example 1

As a protective coating on, for example, wood or metal, the polymers and copolymers of the invention can provide abrasion resistant materials. The polymers and copolymers of the invention can also be useful as a laminate layer in materials such as glass. Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

In wound healing applications, these crosslinked polyurethanes or polyurethane-polyureas provide a transparent wound dressing which exhibits increased modulus compared to dressings made from materials transparant to the final fabric:polymer composite. As a waterproof, breathable membrane, the present crosslinked system adds launderability and dry cleanability to the final fabric.

In regard to their use as magnetic recording media binders, the crosslinked polyurethanes or polyurethane/polyureas of the present invention provide integrity and durability to the magnetic media coating.

The crosslinked polyurethanes or polyurethane-polyureas of the present invention can be useful as flexible magnetic recording media binders; as biomaterials, for example wound dressing films, vascular grafts, and optoelectric devices; lenses, contact lenses and corneal implants; as protective coatings such as antiscratch coatings for wood (furniture) or metal (automobiles); as a tear-resist film, e.g., laminate in glass to prevent shattering; as membranes; and as waterproof, breathable fabric treatments.

Examples of such thermal initiators include peroxides such as benzoyl peroxide, disulfides, and azo compounds such as azobisisobutyronitrile. Examples of such thermal initiators include peroxides such as benzoyl peroxide, disulfides, and azo compounds of such materials as dyed, in the cases where it is intended that the polyurethanes or polyurethane/polyureas described herein be cured with thermal energy, thermal initiators may be combined with the polyurethane/polyurea to increase the thermal reactivity of the system. Polyurethane/polyureas such as thermal initiators may be suitable for such applications such as ferric ion complexes. Examples of typical photosensitizers which may be suitable for such aldehydes, alkyl halides, organometallics, disulfides, benzoin, benzil, organic polyhalides, ketones, which may be suitable for a desired application. Suitable photoinitiators include peroxides, in the cases where such curing is initiated via a photolytic process, such additives may include photoinitiators the corresponds to thermal or photochemical reactivity of such polyurethane/polyurea materials described herein to initiators, may be compounded with the polyurethane or polyurea materials described herein to crosslinked materials will, in general, only swell.

In this invention, the crosslinking is controlled by the amount of 2-glyceryl (meth)acrylate, the nature and/or amount of vinyl monomer(s), the curing conditions (such as level of thermal initiator, level of UV initiator, radiation dose or dose rate), or any combination of the above. Cure is evidenced by decrease in elongation and increased modulus of elasticity of the polyurethanes or polyurethane-polyureas, as well as insolubility in solvents such as dimethylformamide, dimethylacetamide or tetrahydrofuran. Samples that have not been crosslinked or cured will normally dissolve in one of the aforementioned solvents, while insolubility in solvents such as dimethylformamide, dimethylacetamide or tetrahydrofuran. Samples that have not been crosslinked or cured, only swell.

Properties of the polymers, the latter dosage being sufficiently high that it often adversely effects the physical less than 15 megarads, the latter dosage being sufficient to the amount of 1 to 12 megarads.

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TABLE I

Example #	Polymer's Prepared	Macrodiol	Diliscocyanate	Chain extender(s)
3	PTMO-1,000 ^a	MDi ^b	2-GMA ^c	
4	PEO-1,000 ^d	H ₁₂ MDI ^e	2-GMA ^c	
5	PEO-1,000	H ₁₂ MDI	BD/2-GMA (0.9/0.1)	BD/2-GMA (0.95/0.05)
6	PEO-1,000	H ₁₂ MDI	BD/2-GMA (0.5/0.5)	

A solution of the macrodiol, the diisocyanate and the diol in dilute catalyst was refluxed in tetrahydrodioxuran for 3 hours. Then chain extender(s) dissolved in tetrahydrodioxuran was (were) added dropwise following the disappearance of the isocyanate absorption band in the infrared spectrum. The ratio of macrodiol/diisocyanate/chain extender(s) was 1/2/1. When the reaction was complete, thin film samples were prepared by solvent coating the thick polymer solution onto a release liner. The films were then air dried in a hood. Physical data were recorded on films before and after crosslinking. Crosslinking was accomplished by irradiation with an electron beam at 10 Mrads utilizing 150 KV at a web speed of 7.6 meters (25 feet) per minute. Table I lists the polymers prepared and Table II lists the mechanical data obtained.

General Preparation of polyurethanes

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Examples 3-6

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Air was bubbled through a stirred solution of 1.2g of methoxyhydroquinone (MEHQ) in 4 liters of methanol to which was charged 400g of bis(trifluoroacetoxy)methyl) methyl methacrylate and the resultant mixture heated to the temperature of methanol distillation. Continually replacing solvent as it was removed, the solution was heated at this temperature for about 5 hours or until no starting material was evident by nuclear magnetic resonance spectra analysis. The majority of the methanol was removed by residual amounts of solvent were removed utilizing a vacuum pump, providing 165g of a colores, viscous liquid. Structural assignment was confirmed by nuclear magnetic resonance spectra analysis.

Preparation of 2-glyceryl methacrylate

Example 8

England Ultraviolet Co.). The irradiated film was no longer soluble in tetrahydrofuran. Sample was then irradiated for about 15 minutes with an ultraviolet lamp (RUL 3500ATM, Southern New polymer solution was coated onto a sodium chloride infrared plate and the infrared spectrum recorded. The sample (RUL 3500A); the film turned brown and was no longer soluble in tetrahydrofuran. A dilute sample of the approximately 30 minutes with an ultraviolet lamp, available from Southern New England Ultraviolet Co. was added to the thick polymer solution were coated onto a release liner and irradiated for approximately 30 minutes with an infrared lamp with an infrared spectrometer. A dilute sample of the result in the thick polymer solution chromatography to be 143,000 and 45,000. Isocyanate absorption band determined via gel permeation chromatography molecular weights of butanediol dissolved in tetrahydrofuran was added in small quantities following the disappearance of the approximately one half hour at which time 18g of poly(tertramethylene oxide) (number average m.w. for approximately a total volume of about 200ml. Then 4 drops of dibutyltin dilaurate was added followed by refluxing 10.0g (40 mole) of 4,4-diphenylmethane diisocyanate and a sufficient amount of tetrahydrofuran to provide a total volume of about 200ml. The weight and number average molecular weights of the resulting material were determined by infrared spectrum. The weight and number average molecular weights of the result in the infrared spectrum following the irradiation of the sample.

Preparation of polyurethane and crosslinking with UV irradiation

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Example 7

polymer system. This demonstrates that materials of the present invention can be used to prepare a thermoset a hot press. This shows that crosslinking had been effected utilizing a thermal initiator and insoluble in tetrahydrofuran; this formed a film having benzoyl peroxide as a thermal initiator were the AIBN as a thermal initiator and the film formed for solubility in tetrahydrofuran, both the film formed using from the small pieces of thick film was checked for solubility in tetrahydrofuran, both the film formed 10.2 cm (4 inch) diameter ram for approximately 15 minutes. When a very thin film that was thermoformed polyester sheets and put in a hot press at approximately 150°C and about 4,500 kg (5 tons) pressure on a (AIBN) added and (2) with 1% benzoyl peroxide added. Small pieces of both films were placed between two thick films of the polymeric solution of EXAMPLE 6 were made: (1) with 1% azobisisobutyronitrile

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Mechanical Data on Polyurethanes						
Example #		Stress at break	Elongation at break	(psi)	M. Pascals	(%)
3	uncrosslinked	2,600	17.93	1,100	17.93	125
4	crosslinked	670	4.62	320	6.07	540
5	uncrosslinked	530	3.66	320	5.24	260
6	uncrosslinked	330	2.28	770	5.72	80

TABLE II

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To approximately 100 ml of tetrahydrofuran was added 29g (20 moles) of poly(ethylene oxide) diol (number average m. wt appproximately 1300-1600), 10g (40 moles) of 4,4'-diphenylmethane diisocyanate, followed by 4 drops of dibutyl tin dilaurate. The resultant mixture was refluxed for about 0.5 hour, after which time 2-glyceryl methacrylate (approximately 3.2g) was added until the isocyanate absorption peak in the infrared spectrum was no longer visible. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Mechanical data on the films before and after crosslinking showed a very weak polymer before crosslinking with an elongation at break of approximately 150%, whereas after crosslinking the elongation at break was about 60 ± 17% and the stress at break was 13.74 ± 7.38 MPa (1993 ± 1070 psi). This film can be used as a breathable water-repellent fabric treatment.

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To about 150 ml of tetrahydrofuran was added 40.0g of poly(tetramethylene oxide) diol, 3.9g of 4,4'-dicyclohexylmethane diisocyanate and 5 drops of dibutyl tin dilaurate. The resultant mixture was refluxed until the isocyanate peak in the infrared spectrum was no longer evident. Thin films were provided and followed by the addition of 1.0g of 2-glyceryl methacrylate in tetrahydrofuran. The solution was added to the remaining diol solution until two silicone release liners; half of the films were treated with isocyanate and the remainder were left untreated. The samples which were untreated showed a stress at break of 38.48 ± 15.92 MPa (5.580 ± 2.308 pounds per square inch), elongation at break of 720 ± 110%, and moisture vapor transmission of 2,805 ± 221 grams per meter squared per day; the irradiated samples gave a stress at break value of 23.72 ± 3.26 MPa (3.440 ± 472 pounds per square inch), elongation at break of 400%, and moisture vapor transmission of 1672 ± 310 grams per meter squared per day. When checked for solubility, the untreated samples were soluble in tetrahydrofuran, whereas the samples exposed to radiation (crosslinked) were insoluble in tetrahydrofuran.

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The diol prepared in Example 2 was dissolved in tetrahydrofuran to which was added 6.7g (40 moles) of 1,6-diisocyanatohexane and 5 drops of dibutyl tin dilaurate; the resultant mixture was refluxed for about 1 hour. Then 24.4g (40 moles) of poly(tetramethylene oxide) diol (number average m. wt appproximately 610) was added, followed by appproximately 1 hour of reflux at one time. The resultant 4,4'-dicyclohexylmethane diisocyanate in 40 ml of tetrahydrofuran was added at one time. The solution was then refluxed for about 1 hour. Then 1.8g of 1,4-butanediol was added dropwise while monitoring the disappearance of the isocyanate band by infrared spectroscopy. The solution was stirred for about 16 hours at appproximately 20 °C at which time no isocyanate absorption was evident by infrared gel permeation chromatography to be 45,000 and 22,000, respectively. A portion of the thick polymer solution was coated onto a release liner and dried to provide an elastomeric film which was irradiated for about 20 minutes with an ultraviolet lamp (RUL 3500A) at which time the film was found to be insoluble in tetrahydrofuran. The data show that crosslinked polymer films for membrane applications can be prepared by this coating and curing process.

Preparation of mixed diisocyanate polyurethane

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Example 10

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To about 150 ml of tetrahydrofuran was added 40.0g of poly(tetramethylene oxide) diol, 3.9g of 4,4'-dicyclohexylmethane diisocyanate and 5 drops of dibutyl tin dilaurate. The resultant mixture was refluxed until the isocyanate peak in the infrared spectrum was no longer evident. Thin films were provided and followed by the addition of 1.0g of 2-glyceryl methacrylate in tetrahydrofuran. The solution was added to the remaining diol solution until two silicone release liners; half of the films were treated with isocyanate and the remainder were left untreated. The samples which were untreated showed a stress at break of 38.48 ± 15.92 MPa (5.580 ± 2.308 pounds per square inch), elongation at break of 720 ± 110%, and moisture vapor transmission of 2,805 ± 221 grams per meter squared per day; the irradiated samples gave a stress at break value of 23.72 ± 3.26 MPa (3.440 ± 472 pounds per square inch), elongation at break of 400%, and moisture vapor transmission of 1672 ± 310 grams per meter squared per day. When checked for solubility, the untreated samples were soluble in tetrahydrofuran, whereas the samples exposed to radiation (crosslinked) were insoluble in tetrahydrofuran.

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Preparation of aliphatic polyurethane

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Example 9

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To about 150 ml of tetrahydrofuran was added 40.0g of poly(tetramethylene oxide) diol, 3.9g of 4,4'-dicyclohexylmethane diisocyanate and 5 drops of dibutyl tin dilaurate. The resultant mixture was refluxed until the isocyanate peak in the infrared spectrum was no longer visible. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Mechanical data on the films before and after crosslinking showed a very weak polymer before crosslinking with an elongation at break of approximately 150%, whereas after crosslinking the elongation at break was about 60 ± 17% and the stress at break was 13.74 ± 7.38 MPa (1993 ± 1070 psi). This film can be used as a breathable water-repellent fabric treatment.

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To approximately 100 ml of tetrahydrofuran was added 29g (20 moles) of poly(ethylene oxide) diol (number average m. wt appproximately 1300-1600), 10g (40 moles) of 4,4'-diphenylmethane diisocyanate, followed by 4 drops of dibutyl tin dilaurate. The resultant mixture was refluxed for about 0.5 hour, after which time 2-glyceryl methacrylate (approximately 3.2g) was added until the isocyanate absorption peak in the infrared spectrum was no longer visible. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Film thicknesses of 0.023 mm and 0.091 mm were prepared by knifing on release paper and were irradiated with an electron beam [10 Mrads, 150 kV, 7.6 meters (25 feet) per minute with a nitrogen purger]. Mechanical data on the films before and after crosslinking showed a very weak polymer before crosslinking with an elongation at break of approximately 150%, whereas after crosslinking the elongation at break was about 60 ± 17% and the stress at break was 13.74 ± 7.38 MPa (1993 ± 1070 psi). This film can be used as a breathable water-repellent fabric treatment.

Preparation of poly(ethylene oxide) polyurthane

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Using the method of Example 12, one of the four methacrylates listed in Table III was added to the polymeric solution before electron beam treatment. The proportions are given in Table III below. Portions of the resultant polymer solutions (at 29.7% solids in tetrahydrofuran) were coated onto a release liner to give a final dried thickness of about 50.8 micrometers (2 mils) and one half of the samples were irradiated with an accelerated electron beam as detailed in Example 11. All the irradiated films were insoluble in tetrahydrofuran after treatment.

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Example 13 - 18

Preparation of polyether polyurethane

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A mixture of 100g (0.1 mole) of poly(ethylene oxide) diol, 52.47g (0.2 mole) of 4,4'-dicyclohexylmethane diisocyanate and 6 drops of dibutyltin dilaurate in approximately 760ml of tetrahydrofuran were heated to reflux under a nitrogen atmosphere for about 1 hour. To this was added one half of a solution of 8.11g (0.09 mole) of 1,4-butanediol and 1.6g (0.01 mole) of 2-glyceryl methacrylate in about 40ml of tetrahydrofuran. The remainder of the solution was added portionwise at thirty to forty-five minute intervals, monitoring the isocyanate peak in the infrared spectrum; its disappearance was evident after the addition of an additional 8 drops of 1,4-butanediol. The solution was filtered through glass wool to remove a small amount of particulate matter.

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Example 12

Preparation of aromatic polyurethane

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A mixture of 7.0g (20 mole) of bis(trifluoroacetoxy)methyl methacrylate and 0.4g of phenothiazine in 100ml of methanol were refluxed until the volatiles were distilled off as evidenced by the disappearance of the carbon absorption for the trifluoroacetate by infrared analysis. During the distillation fresh methanol was added to maintain at least a 30ml volume in the reaction flask. When distillation was complete, the remaining methanol was removed by evaporation in vacuo and the residue was dissolved in tetrahydrofuran to which was added 10.0g (40 mole) of 4,4'-diphenylmethane diisocyanate plus sufficient tetrahydrofuran to bring the total volume to about 200ml. Poly(ethylene oxide) diol (20.0g) (number average m.w. approximatively 1,000; dried at 100°C under vacuum for about 16 hours) was added and the resultant mixture refluxed for approximately 2 hours at which time the polymer was chain extended by adding a small amount of 1,4-butanediol dropwise while following the isocyanate absorption band by infrared analysis. Portions of the polymeric solution were coated onto two release liners to give final film thicknesses (dried) of both 25.4 micrometers (1 mil) and 330 micrometers (13 mils). Both sets of samples were then irradiated with an accelerated electron beam at 10 Mrads at 7.6 meters (25 feet) per minute at voltage level of 150KV. Additionally some of the 330 micrometers (13 mil) samples were turned over and irradiated with an accelerated electron beam at 10 Mrads at 7.6 meters (25 feet) per minute at voltage level of 200KV. Whereas checked for solubility, the non-irradiated (uncrosslinked) samples were soluble in tetrahydrofuran, whereas the irradiated (crosslinked) samples were insoluble in tetrahydrofuran.

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Example 11

Preparation of aromatic polyurethane

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Example 19

- *CHMA = cyclohexyl methacrylate
- HEMA = 2-hydroxy ethyl methacrylate
- EGDMA = ethylene glycol dimethacrylate
- SIMTA = polydimethylsiloxane dimethacrylate
- PEO = hydroxyl terminated Poly(ethylene oxide)
- H₁₂MDI = methylene diisocyanate (Desmodur W)
- BD = 1,4-butanediol

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Example #	g Solvent	g Polymer	g Methacrylate	PEO* / H ₂ MDI* / BD* / Methacrylate (molar ratios)
13	23.65	5.42	0.60	CHMA
14	24.28	5.56	0.62	HEMA
15	26.86	6.15	0.68	EGDMA
16	25.42	5.82	0.65	SIIMA
17	26.84	6.78	0.75	CHMA
18	24.43	6.17	0.69	SIIMA

TABLE III

55 Example 22

45 A solution of 3.48g (38.6 mmole) of 1,4-butanediol, 0.69 g (4.3 mmoles) of 2-glyceryl methacrylate, 22.5g (85.8 mmoles) of methylene diisocyanate, 200ml of tetrahydrofuran and 5 drops of dibutyltin dilaurate was refluxed one hour. The solution was cooled to room temperature and a solution of a polyether diamine (Jeffamine™ ED600 (25.73g, 42.9 mmoles) in 50ml of isopropyl alcohol was added until the NCO absorption in the infrared spectrum had disappeared. A thin film of this polymer was prepared and irradiated with an electron beam at 5 Mrads and 160KV at a line speed of 7.6 m (25 feet) per minute. After irradiation the polymer film was no longer soluble in tetrahydrofuran/isopropyl alcohol solution or dimethyl acetamide.

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Crosslinkable polyurethane/polyurea containing an oligomeric diamine

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Example 21

35 A solution of 7.8g (30 mmole) of methylene diisocyanate, 14g (14 mmoles) of polytetramethylene oxide glycol (no av. molecular wt, about 1000), 100 ml of tetrahydrofuran and 3 drops of dibutyltin dilaurate was stirred at reflux for 3 hours. Then 1.6g (10 mmoles) of 2-glyceryl methacrylate in 20ml of tetrahydrofuran was added and the solution was refluxed an additional 40 minutes. The solution was cooled in an ice bath and 3.0g of amorphous terminated polydimethylsiloxane (Petrarch Systems cat. no. PS513, viscosity 2,000 cSt) was added. Then a solution of 0.3g of ethylene diamine in 10ml of tetrahydrofuran was added dropwise until the infrared spectrum no longer exhibited an NCO absorption. A thin film of the polymer was prepared and irradiated with 5 Mrads and 160 KV and at a line speed of 7.6 m (25 feet) per min. After irradiation the film was no longer soluble in tetrahydrofuran.

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Crosslinkable polyurethane/polyurea containing silicone

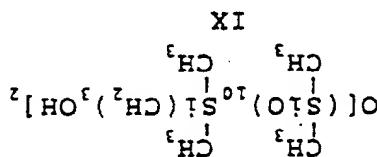
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Example 20

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75 A portion of this polymer solution was added dropwise until the infrared spectra no longer showed an NCO absorption. A portion of this polymer solution was poured onto a silicone release paper, spread to a thin film and air dried. The film was irradiated with an electron beam at 5 Mrads and 160KV at a line speed of 7.6 m (25 feet) per minute. The irradiated film was not soluble in tetrahydrofuran or dimethyl acetamide.

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carbonyl (IX).

5 A solution of 7.8g (30 mmole) of methylene diisocyanate, 8.5g (mmoles) of a silicone

Crosslinkable silicone polyurethane

Crosslinkable polyurethane/polyurea containing ethylene diamine as a chain extender

A solution of 37.5g (37.5 mmoles, 1,000 approx. no. av. molecular weight) poly(ethylene oxide) glycol, 1.13g (12.5 mmoles) of 1,4-butanediol, 2.00g (12.5 mmoles) of 2-glyceryl methacrylate, 19.68g (75.0 mmoles) methylene dicyclohexyl diisocyanate, 5 drops dibutyl tin dilaurate and 200mL of tetrahydrofuran were refluxed three hours. The solution was cooled to room temperature and a solution of 0.75g (12.4 mmoles) of ethylene diamine in 10mL of isopropyl alcohol was added until there was no evidence of NCO absorption by infrared analysis. A polymer film was prepared and irradiated with an electron beam at 5 Mrads and 160 kV at a line speed of 7.6 m (25 feet) per minute. The polymer was no longer soluble in tetrahydrofuran/isopropyl alcohol mixture.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

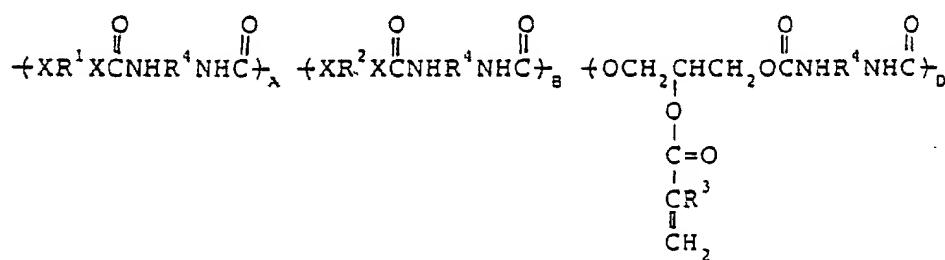
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1. A crosslinkable polyurethane or polyurethane/polyurea comprising the reaction product of a composition comprising a macrodiol or macrodiamine, 2-glyceryl acrylate or 2-glyceryl methacrylate, and a diisocyanate, and optionally at least one of a small glycol or small diamine and a different ethylenically-unsaturated monomer.

2. The polyurethane or polyurethane/polyurea according to claim 1 wherein said macrodiol in said composition is a polyether diol, polyester diol, or silicone carbinol, or wherein said macrodiamine in said composition is a polyether diamine or a polydimethylsiloxane diamine.

3. The polyurethane or polyurethane/polyurea according to claims 1 and 2 wherein said small glycol is an aliphatic, aromatic, or ether glycol containing 2 to 20 carbon atoms, or wherein said small diamine is an aliphatic, aromatic, or ether diamine containing 2 to 20 carbon atoms.

4. A crosslinkable polyurethane or polyurethane/polyurea having randomly disposed units of the formula



40 wherein:

X is -NH- or -O-

R^1 is a polyether, a polyester, or a polydimethylsiloxane segment.

R^2 and R^4 independently are selected from the class consisting of alkylene, cycloalkylene, and arylene groups and combinations thereof.

⁴⁵ B³ is H or CH₃, and

A, B, D = total number of OH and NH equivalents

5. The polyurethane or polyurethane/polyurea according to claims 1 to 4 which has been crosslinked by means of at least one of thermal energy, ultraviolet radiation, gamma radiation, or electron beam radiation.

50 6. The crosslinked polyurethane or polyurethane/polyurea according to claim 5 which is a flexible magnetic recording media binder, a biomaterial, a membrane, a fabric treatment, or a protective coating.

7. The crosslinked polyurethane or polyurethane/polyurea according to claims 5 and 6 which is a wound dressing, a vascular graft, or an ophthalmic device.

8. The crosslinked polyurethane or polyurethane/polyurea according to claims 5 and 6 which is a waterproof, breathable fabric treatment.

9. A method comprising the step of

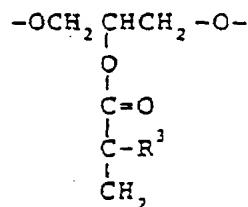
a) reacting a macrodiol or macrodiamine, a diisocyanate, 2-glyceryl acrylate or 2-glyceryl methacrylate and optionally at least one of a small glycol, a small diamine, and an ethylenically-unsaturated monomer to provide a crosslinkable polyurethane or polyurethane/polyurea.

10. The method according to claim 9 further comprising the step of

b) effecting crosslinking of said polyurethane or polyurethane/polyurea by means of at least one of thermal energy, ultraviolet radiation, gamma radiation, and electron beam radiation.

11. A method for adjusting the crosslinking of polyurethanes or polyurethane/polyureas comprising the
5 steps of:

a) providing a crosslinkable polyurethane or polyurethane/polyurea having chain extender units of the formula



10 wherein R³ is hydrogen or methyl, and

20 b) crosslinking said polyurethane via at least one of thermal energy, ultraviolet radiation, gamma radiation or electron beam radiation.

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(54) Polyurethanes and polyurethane/polyureas crosslinked using 2-glyceryl acrylate or 2-glyceryl methacrylate.

(57) A crosslinkable polyurethane or polyurethane/polyurea comprises the reaction product of a composition comprising a macrodioiol or macrodiacamine, 2-glyceryl acrylate or 2-glyceryl methacrylate, a diisocyanate, and optionally a small glycol or small diamine as chain extender. The performance properties of the polyurethanes and polyurethane/polyureas can be controlled by adjustment of the crosslink level and/or curing parameters.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 5312

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 040 151 (SOCIETE NATIONALE DES POU DRES) * Claims 1,4,7; page 9, lines 4-31; page 13, lines 1-32* & US-A-4 366 301 (Cat. D) ---	1	C 08 G 18/67 A 61 L 27/00 A 61 L 15/00 G 02 B 1/04 C 09 D 3/72 D 06 M 15/564 B 01 D 13/04 G 11 B 5/702
A	FR-A-1 366 079 (CHEMICAL INVESTORS) * Page 1; left-hand column, paragraph 1; right-hand column, paragraph 3 * -----	1	
TECHNICAL FIELDS SEARCHED (Int. Cl.4)			
C 08 G			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	31-10-1988	VAN PUYMBROECK M.A.	
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